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(±)-3-Oxocyclohexanecarboxylic and -acetic acids: contrasting hydrogen-bonding patterns in two homologous keto acids

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The crystal structures for the title compounds reveal fundamentally different hydrogen-bonding patterns. (±)-3-Oxocyclohexanecarboxylic acid, $C_7H_{10}O_3$, displays acid-to-ketone catemers having a glide relationship for successive components of the hydrogen-bonding chains which advance simultaneously by two cells in *a* and one in *c* [O···O = 2.683 (3) Å and O—H···O = 166°]. A pair of intermolecular close contacts exists involving the acid carbonyl group. The asymmetric unit in (±)-3-oxocyclohexaneacetic acid, $C_8H_{12}O_3$, utilizes only one of two available isoenthalpic conformers and its aggregation involves mutual hydrogen bonding by centrosymmetric carboxyl dimerization [O···O = 2.648 (3) Å and O—H···O = 171°]. Intermolecular close contacts exist for both the ketone and the acid carbonyl group.

Comment

Five hydrogen-bonding modes are known for the crystalline keto carboxylic acids our studies concern. Two of these lack ketone involvement, reflecting the common pairing and much rarer chain modes known for simple acids (Leiserowitz, 1976). Acid-to-ketone chains (catemers) constitute a sizable minority of cases, while intramolecular hydrogen bonds and acid-to-ketone dimers are rarely observed. Hydrates with more complex hydrogen-bonding patterns also exist. We have previously provided examples of many of these, along with discussions of the factors that appear to govern the choice of mode (Brunskill *et al.*, 1999; Lalancette *et al.*, 1998).

We report here the structure and hydrogen-bonding behavior of the title compounds, *i.e.* γ-keto acid (I) and its δ- homolog (II). Both γ- and δ-keto acids are rich in hydrogen-bonding types, embracing not only dimers, but catemers of both the homo- and heterochiral type, and internal hydrogen bonds, as well as hydrated patterns. Compounds (I) and (II) were both of interest to us due to their relationships to several keto acids whose crystal structures display unusual conformational (Lalancette & Thompson, 2001) or hydrogen-bonding arrangements (Barcon *et al.*, 1998).

(I) (II)

Fig. 1 shows the asymmetric unit of (I) with its atom-numbering scheme. Given the expected chair conformation, the only rotational option involves the equatorial acid group, which is turned with its carbonyl toward the C1—C2 bond so that torsion angle O2—C7—C1—C2 is 19.1 (3)°. The intramolecular dihedral angle between the carboxyl and ketone planes is 65.60 (12)°. The disordering of C—O bond lengths and C—C—O angles often observed in dimerically hydrogen-bonded acids (Leiserowitz, 1976) does not appear in catemers, whose geometry cannot support the averaging mechanisms involved. Hence, in (I), which is catemeric, these C—O bond lengths are 1.191 (3)/1.324 (3) Å, with angles of 125.4 (2)/111.76 (19)°. Our own survey of 56 keto acid structures that are not acid dimers gives average values of 1.200 (11)/1.32 (2) Å and 124.5 (14)/112.7 (17)°.

Fig. 2 shows the cell packing, in which alternating glide-related molecules associate in carboxyl-to-ketone hydrogen-bonding catemers, with two such chains passing counter-directionally through the cell. We categorize the relationships of intrachain units in catemers as homochiral (screw- or translationally related) or heterochiral (glide-related), and for keto-acid catemers overall, the observed order of prevalence is: screw > translation > glide. Such heterochiral catemers are often much more flattened and ribbon-like than helices, as they are here, with the rings splayed out alternately to either side of the hydrogen-bonding axis. Relative to the cell chosen for (I), the chains follow no crystallographic axis but, with each full hydrogen-bonding cycle, advance simultaneously by two cells in *a* and one in *c*. The arrangement bears a striking resemblance to that found for the α,β-unsaturated counterpart of (I) (Barcon *et al.*, 1998).

The intermolecular dihedral angle between the carboxyl and ketone planes in hydrogen-bonded molecules is 65.05 (12)°. To characterize the geometry of hydrogen bonding to carbonyls, we use a combination of the H···O=C angle and the H···O=C—C torsion angle. These describe the approach of the acid H atom to the O atom in terms of its

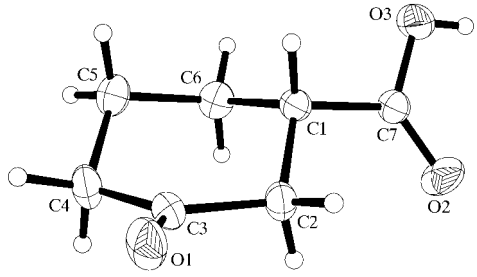

Figure 1
The asymmetric unit of (I), with the atom numbering. Displacement ellipsoids are drawn at the 20% probability level.

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deviation from, respectively, C═O axiality (ideal = 120°) and coplanarity with the carbonyl (ideal = 0°). In (I), these angles are 128.5 and 2.6°, respectively.

Within the 2.7 Å range we usually employ for non-bonded H···O packing interactions (Steiner, 1997), a pair of intermolecular C—H···O close contacts exists for the acid carbonyl, involving H1 (2.50 Å) and H5*A* (2.64 Å) in the same neighbor, glide-related in *c*. Using compiled data for a large number of C—H···O contacts, Steiner & Desiraju (1998) have found significant statistical directionality as far out as 3.0 Å, and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

Among several factors tending to disfavor standard dimeric carboxyl hydrogen bonding, we have identified low availability of alternative conformations. The flexibility associated with cyclohexane rings is a solution characteristic; in the crystal, the strong preference for chair conformations and equatorial substituents actually leaves a system like (I) with very few conformational options. As a result, (I) joins a number of nominally flexible cyclic molecules that behave much more like rigid systems and adopt catemeric hydrogen-bonding modes.

Fig. 3 shows the asymmetric unit of (II) with its atom-numbering scheme. The one-carbon lengthening of the equatorial side-chain produces more conformational options than in (I), notably those involving rotation about C1—C7. The observed conformer has a staggered arrangement about this bond [torsion angle C8—C7—C1—C2 = −174.9 (2)°], with a single *gauche* interaction involving C6 and C8. Its alternative, differing by 120° of C1—C7 rotation has a comparable *gauche* interaction juxtaposing C2 and C8, but with a calculated enthalpy negligibly different from the one shown. The packing arrangement for (II) chooses only one of these two isoenthalpic conformations, as opposed to the analogous case of (±)-3-oxocyclohexanepropionic acid (Lalancette & Thompson, 2001), where both appear in the asymmetric unit. The intramolecular dihedral angle between the carboxyl and ketone planes in (II) is 83.43 (9)°.

Values cited as typical for highly ordered dimeric carboxyls are 1.21/1.31 Å and 123/112° (Borthwick, 1980). The carboxyl

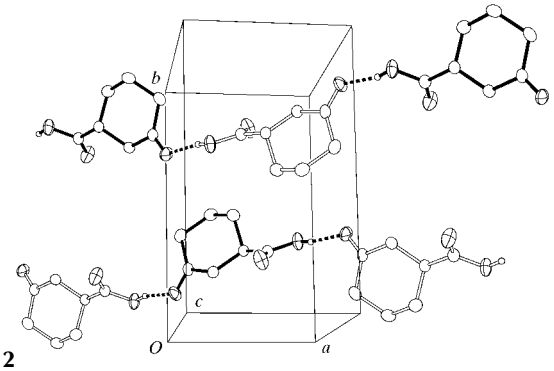

Figure 2
A packing diagram for (I) with extracellular molecules to show the two heterochiral hydrogen-bonding chains passing counterdirectionally through the cell. The handedness of the molecules is differentiated by the shading of the bonds, and all carbon-bound H atoms have been removed for clarity. Displacement ellipsoids are set at the 20% probability level.

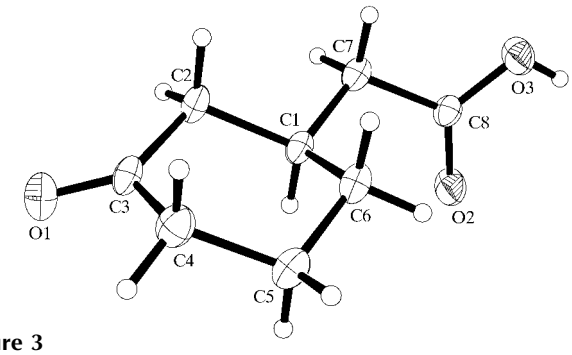

Figure 3
The asymmetric unit of (II), with the atom numbering. Displacement ellipsoids are drawn at the 20% probability level.

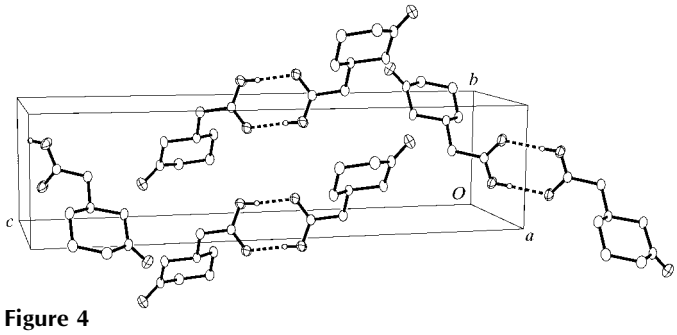

Figure 4
A partial packing diagram for (II), with an extracellular molecule, illustrating the dimers centered on the *ac* face and on the *b* edge of the chosen cell. Carbon-bound H atoms have been removed for clarity. Displacement ellipsoids are set at the 20% probability level.

C—O distances and C—C—O angles found for (II) [1.232 (3)/1.269 (3) Å and 121.0 (2)/116.0 (2)°] suggest significant disordering. Although we were unable to find electron density for partial H atoms consistent with this disorder in electron-density difference maps, a single hydrogen was found in the correct position relative to O3.

Fig. 4 shows the packing arrangement, involving centrosymmetric dimers centered on the *ac* face and on the *b* edge of the chosen cell. Intermolecular C—H···O close contacts were found both for the acid carbonyl (2.70 Å to H5*A* in a neighbor translationally related in *a*) and for the ketone (2.67 Å to H4*B* and 2.58 Å to H7*A* in separate glide-related contacts to molecules mutually related by translation).

In a pattern typical for catemeric keto acids, the solid-state (KBr) IR spectrum of (I) has well separated C═O absorptions at 1728 and 1686 cm^{-1}, consistent with shifts produced when hydrogen bonding is, respectively, removed from a carboxyl and added to a ketone C═O group. In $CHCl_3$ solution, these two peaks coalesce to a single peak centered around 1713 cm^{-1}. Consistent with its dimeric character, compound (II) in KBr has a single peak at 1695 cm^{-1} for both C═O groups; in $CHCl_3$, this single peak appears at 1710 cm^{-1}.

Experimental

Compound (I) was prepared by Pd-catalyzed hydrogenation of 3-oxo-1-cyclohexene-1-carboxylic acid (Barcon *et al.*, 1998). The crystal used was obtained from Et_2O (m.p. 344 K). For (II), Rh-catalyzed hydrogenation of 3-hydroxyphenylacetic acid, followed by Jones oxidation, yielded material suitable for X-ray after recrystallization from Et_2O/hexane (m.p. 351 K).

Compound (I)

Crystal data

$C_7H_{10}O_3$
M_r = 142.15
Monoclinic, $P2_1/c$
a = 6.3346 (17) Å
b = 10.758 (3) Å
c = 11.012 (3) Å
β = 94.202 (17)°
V = 748.4 (4) Å^3
Z = 4
D_x = 1.262 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
θ = 6.1–15.5°
μ = 0.10 mm^{-1}
T = 296 (2) K
Parallelepiped, colorless
0.40 × 0.30 × 0.20 mm

Data collection

Siemens $P4$ diffractometer
$2\theta/\theta$ scans
1891 measured reflections
1315 independent reflections
854 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 25°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 13$
3 standard reflections
every 97 reflections
intensity decay: variation <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.122
S = 1.04
1315 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.2077P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.00
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O2—C7	1.191 (3)	O3—C7	1.324 (3)
O2—C7—C1	125.4 (2)	O3—C7—C1	111.76 (19)
C2—C1—C7—O2	19.1 (3)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.82	1.89	2.683 (3)	166

Symmetry code: (i) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$.

Compound (II)

Crystal data

$C_8H_{12}O_3$
M_r = 156.18
Monoclinic, $P2_1/n$
a = 6.625 (2) Å
b = 5.6690 (10) Å
c = 21.841 (5) Å
β = 90.33 (2)°
V = 820.3 (3) Å^3
Z = 4
D_x = 1.265 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
θ = 7.5–13.0°
μ = 0.10 mm^{-1}
T = 241 (2) K
Parallelepiped, colorless
0.50 × 0.40 × 0.33 mm

Data collection

Siemens $P4$ diffractometer
$2\theta/\theta$ scans
2238 measured reflections
1447 independent reflections
989 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 25$
3 standard reflections
every 97 reflections
intensity decay: variation <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.143
S = 1.01
1447 reflections
101 parameters
H atoms parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.2424P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O2—C8	1.232 (3)	O3—C8	1.269 (3)
O2—C8—C7	121.0 (2)	O3—C8—C7	116.0 (2)
C2—C1—C7—C8	−174.9 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2^{i}	0.83	1.83	2.648 (3)	171

Symmetry code: (i) $2-x, 1-y, -z$.

All H atoms for compounds (I) and (II) were found in electron-density difference maps. For (I), the H atoms were placed in calculated positions and allowed to refine as riding models on their respective C and O atoms, with the methine H atom fixed at 0.98 Å, methylene-H atoms at 0.97 Å and OH at 0.82 Å; the displacement parameters for all of the H atoms were allowed to refine, except for the carboxyl H atom, which was set at 150% of the displacement parameter of its O atom. For (II), the H atoms were placed in calculated postions with the methine H atom fixed at 0.99 Å, the methylene-H atoms at 0.98 Å and the OH at 0.83 Å. For (II), the displacement parameters for the C-bound H atoms were set at 120% of their respective atoms, while the carboxyl-H atom was set at 150% of the displacement parameter of its O atom.

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1356). Services for accessing these data are described at the back of the journal.

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